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(54) **Method for preparing rare earth permanent magnet material**

(57) A rare earth permanent magnet material is prepared by covering a sintered magnet body of R¹-Fe-B composition wherein R¹ is a rare earth element, with a powder comprising at least 30% by weight of an alloy of R²_aT_bM_cA_dH_e wherein R² is a rare earth element, T is Fe and/or Co, and M is Al, Cu or the like, and having an

average particle size up to 100 μm, and heat treating the powder-covered magnet body at a suitable temperature, for causing R², T, M and A in the powder to be absorbed in the magnet body.

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Description

[0001] This invention relates to methods for preparing R-Fe-B permanent magnet materials. Particular concerns are to provide a good or enhanced coercive force while maintaining, or minimizing a decline of, the remanence.

BACKGROUND

[0002] By virtue of excellent magnetic properties, Nd-Fe-B permanent magnets find an ever increasing range of application. The recent challenge to the environmental problem has expanded the application range of magnets to industrial equipment, electronic automobiles and wind power generators. It is required to further improve the performance of R-Fe-B magnets such as Nd-Fe-B magnets.

[0003] Indexes for the performance of magnets include remanence (or residual magnetic flux density) and coercive force. An increase in the remanence of Nd-Fe-B sintered magnets can be achieved by increasing the volume factor of $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound and improving the crystal orientation. To this end, a number of modifications have been made on the process. For increasing coercive force, there are known different approaches including grain refinement, the use of alloy compositions with greater Nd contents, and the addition of effective elements. The currently most common approach is to use alloy compositions having Dy or Tb substituted for part of Nd. Substituting these elements for Nd in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound increases both the anisotropic magnetic field and the coercive force of the compound. The substitution with Dy or Tb, on the other hand, reduces the saturation magnetic polarization of the compound. Therefore, as long as the above approach is taken to increase coercive force, a loss of remanence is unavoidable. Since Tb and Dy are expensive metals, it is desired to minimize their addition amount.

[0004] In Nd-Fe-B magnets, the coercive force is given by the magnitude of an external magnetic field which creates nuclei of reverse magnetic domains at grain boundaries. Formation of nuclei of reverse magnetic domains is largely dictated by the structure of the grain boundary in such a manner that any disorder of grain structure in proximity to the boundary invites a disturbance of magnetic structure or a decline of magneto-crystalline anisotropy, helping formation of reverse magnetic domains. It is generally believed that a magnetic structure extending from the grain boundary to a depth of about 5 nm contributes to an increase of coercive force, that is, the magneto-crystalline anisotropy is reduced in this region. It is difficult to acquire a morphology effective for increasing coercive force.

[0005] For further information see JP-B 5-31807, JP-A 5-21218,

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K.T. Park, K. Hiraga and M. Sagawa, "Effect of Metal-Coating and Consecutive Heat Treatment on Coercivity of Thin Nd-Fe-B Sintered Magnets," Proceedings of the Sixteen International Workshop on Rare-Earth Magnets and Their Applications, Sendai, p.257 (2000), and

K. Machida, H. Kawasaki, M. Ito and T. Horikawa, "Grain Boundary Tailoring of Nd-Fe-B Sintered Magnets and Their Magnetic Properties," Proceedings of the 2004 Spring Meeting of the Powder & Powder Metallurgy Society, p.202.

[0006] An aim herein is to provide new and useful methods for preparing rare earth permanent magnets of R-Fe-B sintered type (wherein R is two or more elements selected from rare earth elements inclusive of Sc and Y), the magnet exhibiting high performance, preferably reducing reliance on Tb and Dy.

[0007] The inventors have discovered that when a $\text{R}^1\text{-Fe-B}$ sintered magnet (wherein R^1 is at least one element selected from rare earth elements inclusive of Sc and Y), typically a Nd-Fe-B sintered magnet, with a rare earth-rich alloy powder which becomes a liquid phase at the treating temperature being disposed on a surface thereof, is heated at a temperature below the sintering temperature, R^2 contained in the powder is effectively absorbed in the magnet body so that R^2 is concentrated only in proximity to grain boundaries for modifying the structure in proximity to the grain boundaries to restore or enhance magneto-crystalline anisotropy whereby the coercive force is increased while suppressing a decline of remanence.

[0008] The invention provides a method for preparing a rare earth permanent magnet material, comprising the steps of:

disposing a powder on a surface of a sintered magnet body of $\text{R}^1\text{-Fe-B}$ composition wherein R^1 is at least one element selected from rare earth elements inclusive of Sc and Y, said powder comprising at least 30% by weight of an alloy of $\text{R}^2_a\text{T}_b\text{M}_c\text{A}_d\text{H}_e$ wherein R^2 is at least one element selected from rare earth elements inclusive of Sc and Y, T is iron and/or cobalt, M is at least one element selected from the group consisting of Al, Cu, Zn, In, Si, P, S, Ti, V, Cr, Mn, Ni, Ga, Ge, Zr, Nb, Mo, Pd, Ag, Cd, Sn, Sb, Hf, Ta, and W, A is boron and/or carbon, H is hydrogen, and "a" to "e" indicative of atomic percentages based on the alloy are in the range: $15 \leq a \leq 80$, $0.1 \leq c \leq 15$, $0 \leq d \leq 30$, $0 \leq e \leq (a \times 2.5)$, and the balance of b, and said powder having an average particle size equal to or less than $100 \mu\text{m}$, and

heat treating the magnet body having the powder disposed on its surface at a temperature equal to or below the sintering temperature of the magnet body in vacuum or in an inert gas, for absorption treatment for causing R^2 and

at least one of T, M and A in the powder to be absorbed in the magnet body.

[0009] In a preferred embodiment, the sintered magnet body has a minimum portion with a dimension equal to or less than 20 mm.

5 **[0010]** In a preferred embodiment, the powder is disposed on the magnet body surface in an amount corresponding to an average filling factor of at least 10% by volume in a magnet body-surrounding space at a distance equal to or less than 1 mm from the magnet body surface.

10 **[0011]** In a preferred embodiment, the powder contains at least 1% by weight of at least one of an oxide of R³, a fluoride of R⁴, and an oxyfluoride of R⁵ wherein each of R³, R⁴, and R⁵ is at least one element selected from rare earth elements inclusive of Sc and Y, so that at least one of R³, R⁴, and R⁵ is absorbed in the magnet body. Preferably, each of R³, R⁴, and R⁵ contains at least 10 atom% of at least one element selected from Nd, Pr, Dy, and Tb.

[0012] In a preferred embodiment, R² contains at least 10 atom% of at least one element selected from Nd, Pr, Dy, and Tb. In a preferred embodiment, the disposing step includes feeding the powder as a slurry dispersed in an aqueous or organic solvent.

15 **[0013]** The method may further comprise, after the absorption treatment, the step of effecting aging treatment at a lower temperature. The method may further comprise, prior to the disposing step, the step of washing the magnet body with at least one agent selected from alkalis, acids, and organic solvents. The method may further comprise, prior to the disposing step, the step of shot blasting the magnet body for removing a surface layer. The method may further comprise the step of washing the magnet body with at least one agent selected from alkalis, acids, and organic solvents after the absorption treatment or after the aging treatment. The method may further comprise the step of machining the magnet body after the absorption treatment or after the aging treatment. The method may further comprise the step of plating or coating the magnet body, after the absorption treatment, after the aging treatment, after the alkali, acid or organic solvent washing step following the aging treatment, or after the machining step following the aging treatment.

25 BENEFITS

[0014] We find that rare earth permanent magnet materials in the form of R-Fe-B sintered magnets made by the present methods exhibit high performance (coercivity and remanence) even with a low content of Tb or Dy.

30 FURTHER EXPLANATIONS; OPTIONS AND PREFERENCES

[0015] The invention pertains to an R-Fe-B sintered magnet material exhibiting high performance and preferably having a minimized content of Tb or Dy.

35 **[0016]** The invention starts with an R¹-Fe-B sintered magnet body which is obtainable e.g. from a mother alloy by a standard procedure including crushing, fine pulverization, compaction and sintering.

[0017] As used herein, R and R¹ are selected from rare earth elements inclusive of Sc and Y. R mainly refers to the finished magnet body while R¹ is mainly used for the starting material.

40 **[0018]** The mother alloy contains R¹, T, A and optionally E. R¹ is at least one element selected from rare earth elements inclusive of Sc and Y, specifically from among Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu, with Nd, Pr and Dy being preferably predominant. It is preferred that rare earth elements inclusive of Sc and Y account for 10 to 15 atom%, more preferably 12 to 15 atom% of the overall alloy. Desirably R¹ contains at least 10 atom%, especially at least 50 atom% of Nd and/or Pr based on the entire R¹. T is iron (Fe) and/or cobalt (Co). The content of Fe is preferably at least 50 atom%, especially at least 65 atom% of the overall alloy. A is boron (B) and/or carbon (C). It is preferred that boron accounts for 2 to 15 atom%, more preferably 3 to 8 atom% of the overall alloy. E is at least one element selected from the group consisting of Al, Cu, Zn, In, Si, P, S, Ti, V, Cr, Mn, Ni, Ga, Ge, Zr, Nb, Mo, Pd, Ag, Cd, Sn, Sb, Hf, Ta, and W, and may be contained in an amount of 0 to 11 atom%, especially 0.1 to 5 atom% of the overall alloy. The balance consists of incidental impurities such as nitrogen (N), oxygen (O) and hydrogen (H), and their total is generally equal to or less than 4 atom%.

45 **[0019]** The mother alloy is suitably prepared by melting metal or alloy feeds in vacuum or an inert gas atmosphere, preferably argon atmosphere, and casting the melt into a flat mold or book mold or strip casting. A possible alternative is a so-called two-alloy process involving separately preparing an alloy approximate to the R¹₂Fe₁₄B compound composition constituting the primary phase of the relevant alloy and a rare earth-rich alloy serving as a liquid phase aid at the sintering temperature, crushing, then weighing and mixing them. Notably, the alloy approximate to the primary phase composition is subjected to homogenizing treatment, if necessary, for the purpose of increasing the amount of the R¹₂Fe₁₄B compound phase, since primary crystal α -Fe is likely to be left depending on the cooling rate during casting and the alloy composition. The homogenizing treatment is a heat treatment at 700 to 1,200°C for at least one hour in vacuum or in an Ar atmosphere. To the rare earth-rich alloy serving as a liquid phase aid, the melt quenching and strip casting techniques are applicable as well as the above-described casting technique.

[0020] The alloy is generally crushed to a size of 0.05 to 3 mm, especially 0.05 to 1.5 mm. The crushing step uses e.g. a Brown mill or hydriding pulverization, with the hydriding pulverization being preferred for those alloys as strip cast. The coarse powder is then finely divided to a size of 0.2 to 30 μm , especially 0.5 to 20 μm , for example, by a jet mill using nitrogen under pressure.

[0021] The fine powder is compacted on a compression molding machine while being oriented under a magnetic field. The green compact is placed in a sintering furnace where it is sintered in vacuum or in an inert gas atmosphere usually at a temperature of 900 to 1,250°C, preferably 1,000 to 1,100°C. The sintered magnet thus obtained contains 60 to 99% by volume, preferably 80 to 98% by volume of the tetragonal $\text{R}^1_2\text{Fe}_{14}\text{B}$ compound as the primary phase, with the balance being 0.5 to 20% by volume of a rare earth-rich phase, 0 to 10% by volume of a B-rich phase, and 0.1 to 10% by volume of at least one of rare earth oxides, and carbides, nitrides and hydroxides resulting from incidental impurities, or a mixture or composite thereof.

[0022] The sintered block is then machined into a predetermined shape. It is noted that M and/or R^2 to be absorbed in the magnet body according to the invention is fed from the magnet body surface wherein R^2 is at least one element selected from rare earth elements inclusive of Sc and Y, specifically from among Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu, with Nd, Pr and Dy being preferably predominant. If the magnet body is too large in dimensions, the objects are not achievable. Then, the sintered block is preferably machined to a shape having a minimum portion with a dimension equal to or less than 20 mm, more preferably of 0.1 to 10 mm. (Thus, in a preferred machined shape, all points lie on at least one through-dimension equal to or less than 20mm, preferably 0.1 to 10mm.) Also preferably, the shape includes a maximum portion having a dimension of 0.1 to 200 mm, especially 0.2 to 150 mm. Any appropriate shape may be selected. For example, the block may be machined into a plate or cylindrical shape.

[0023] Then a powder is disposed on a surface of the sintered magnet body. The powder contains at least 30% by weight of an alloy of $\text{R}^2_a\text{T}_b\text{M}_c\text{A}_d\text{H}_e$ wherein R^2 is at least one element selected from rare earth elements inclusive of Sc and Y, T is iron and/or cobalt, M is at least one element selected from the group consisting of Al, Cu, Zn, In, Si, P, S, Ti, V, Cr, Mn, Ni, Ga, Ge, Zr, Nb, Mo, Pd, Ag, Cd, Sn, Sb, Hf, Ta, and W, A is boron and/or carbon, H is hydrogen, and "a" to "e" indicative of atomic percentages based on the alloy are in the range: $15 \leq a \leq 80$, $0.1 \leq c \leq 15$, $0 \leq d \leq 30$, $0 \leq e \leq (a \times 2.5)$, and the balance of b. The powder has an average particle size equal to or less than 100 μm . The magnet body with the powder on its surface is heat treated at a temperature equal to or below the sintering temperature of the magnet body in vacuum or in an inert gas such as Ar or He. This heat treatment is referred to as absorption treatment, hereinafter. The absorption treatment causes R^2 to be absorbed in the magnet body mainly through the grain boundary phase. Since R^2 being absorbed gives rise to substitution reaction with $\text{R}^1_2\text{Fe}_{14}\text{B}$ grains in proximity to grain boundaries, R^2 is preferably selected such that it does not reduce the magneto-crystalline anisotropy of $\text{R}^1_2\text{Fe}_{14}\text{B}$ grains. It is then preferred that at least one of Pr, Nd, Tb and Dy be predominant in R^2 . The alloy may be prepared by melting metal or alloy feeds in vacuum or an inert gas atmosphere, preferably argon atmosphere, and casting the melt into a flat mold or book mold, melt quenching or strip casting. The alloy has a composition approximate to the liquid phase alloy in the above-described two-alloy process.

[0024] It is preferred that at least 10 atom% of R^2 be selected from (i.e. at least one of) Pr, Nd, Tb and Dy, more preferably at least 20 atom%, even more preferably at least 40 atom% of at least one of Pr, Nd, Tb and Dy, up to and including 100 atom%.

[0025] The preferred range of a, c, d, and e is $15 \leq a \leq 70$, $0.1 \leq c \leq 10$, $0 \leq d \leq 15$, and $0 \leq e \leq (a \times 2.3)$, and more preferably $20 \leq a \leq 50$, $0.2 \leq c \leq 8$, $0.5 \leq d \leq 12$, and $0.1 \leq e \leq (a \times 2.1)$. Herein, b is preferably from 10 to 90, more preferably from 15 to 80, even more preferably from 15 to 75. T is iron (Fe) and/or cobalt (Co) while the content of Fe is preferably 30 to 70 atom%, especially 40 to 60 atom% based on T. A is boron (B) and/or carbon (C) while the content of boron is preferably 80 to 100 atom%, especially 90 to 99 atom% based on A.

[0026] The alloy $\text{R}^2_a\text{T}_b\text{M}_c\text{A}_d\text{H}_e$ is generally crushed to a size of 0.05 to 3 mm, especially 0.05 to 1.5 mm. Suitable crushing uses a Brown mill or hydriding pulverisation, with the hydriding pulverisation being preferred for those alloys as strip cast. The coarse powder is then finely divided, for example, by a jet mill using nitrogen under pressure. For the reason that the smaller the particle size of the powder, the higher becomes the absorption efficiency, the fine powder preferably has a maximum particle size not more than 500 μm , more preferably not more than 300 μm , and even more preferably not more than 100 μm . The lower limit of minimum particle size is preferably 0.1 μm , more preferably at least 0.5 μm though not particularly restricted. The average particle size is not more than 100 μm , preferably not more than 50 μm , more preferably not more than 20 μm . Preferably it is at least 1 μm . The average particle size is determined as a weight average diameter D_{50} (particle diameter at 50% by weight cumulative, or median diameter), measuring the particle size distribution by laser diffractometry.

[0027] The powder contains at least 30% by weight, especially at least 60% by weight of the alloy, with even 100% by weight being acceptable, while the powder may contain at least one of an oxide of R^3 , a fluoride of R^4 , and an oxyfluoride of R^5 in addition to the alloy. Herein R^3 , R^4 , and R^5 are selected from rare earth elements inclusive of Sc and Y, with illustrative examples of R^3 , R^4 , and R^5 being the same as R^1 .

[0028] The oxide of R^3 , fluoride of R^4 , and oxyfluoride of R^5 used herein are typically R^3_2O_3 , R^4F_3 , and R^5OF , re-

spectively. They generally refer to oxides containing R³ and oxygen, fluorides containing R⁴ and fluorine, and oxyfluorides containing R⁵, oxygen and fluorine, including R³O_n, R⁴F_n, and R⁵O_mF_n wherein m and n are arbitrary positive numbers, and modified forms in which part of R³, R⁴ or R⁵ is substituted or stabilized with another metal element in line with the skilled person's knowledge, as long as they do not lose the described benefits of the proposed method.

5 **[0029]** It is preferred that at least 10 atom%, more preferably at least 20 atom%, of any or each of R³, R⁴ and R⁵ that is used, be selected from Pr, Nd, Tb and Dy, even up to and including 100 atom%.

[0030] Preferably the oxide of R³, fluoride of R⁴, and oxyfluoride of R⁵ have an average particle size equal to or less than 100 μm, more preferably 0.001 to 50 μm, and even more preferably 0.01 to 10 μm.

10 **[0031]** The content of the oxide of R³, fluoride of R⁴, and oxyfluoride of R⁵ is preferably at least 0.1% by weight, more preferably 0.1 to 50% by weight, and even more preferably 0.5 to 25% by weight based on the powder.

[0032] If necessary, boron, boron nitride, silicon or carbon in microparticulate form or an organic compound such as stearic acid may be added to the powder for the purposes of improving the dispersibility or enhancing the chemical and physical adsorption of the powder particles.

15 **[0033]** For the reason that a more amount of R is absorbed as the filling factor of the powder in the magnet surface-surrounding space is higher, the filling factor should be at least 10% by volume, preferably at least 40% by volume, calculated as an average value in the magnet surrounding space from the magnet surface to a distance equal to or less than 1 mm, in order for the invention to attain its effect. The upper limit of filling factor is generally equal to or less than 95% by volume, and especially equal to or less than 90% by volume, though not particularly restrictive.

20 **[0034]** One exemplary technique of disposing or applying the powder is by dispersing the powder in water or an organic solvent to form a slurry, immersing the magnet body in the slurry, and drying in hot air or in vacuum or drying in the ambient air. Alternatively, the powder can be applied by spray coating or the like. Any such technique is characterized by ease of application and mass treatment. Specifically the slurry contains the powder in a concentration of 1 to 90% by weight, more specifically 5 to 70% by weight.

25 **[0035]** The temperature of absorption treatment is equal to or below the sintering temperature of the magnet body. The treatment temperature is limited for the following reason. If treatment is done at a temperature above the sintering temperature (designated T_s in °C) of the relevant sintered magnet, there arise problems like (1) the sintered magnet alters its structure and fails to provide excellent magnetic properties; (2) the sintered magnet fails to maintain its dimensions as worked due to thermal deformation; and (3) the diffusing R can diffuse into the interior of magnet grains beyond the grain boundaries in the magnet, resulting in a reduced remanence. The treatment temperature should thus be equal
30 to or below the sintering temperature, and preferably equal to or below (T_s-10)°C. The lower limit of temperature is preferably at least 210°C, more preferably at least 360°C. The time of absorption treatment is from 1 minute to 10 hours. The absorption treatment is not completed within less than 1 minutes whereas more than 10 hours of treatment gives rise to the problems that the sintered magnet alters its structure and the inevitable oxidation and evaporation of components adversely affect the magnetic properties. The more preferred time is 5 minutes to 8 hours, especially 10 minutes
35 to 6 hours.

[0036] Also preferably, the absorption treatment is followed by aging treatment. The aging treatment is desirably at a temperature which is below the absorption treatment temperature, preferably from 200°C to a temperature lower than the absorption treatment temperature by 10°C, and more preferably from 350°C to a temperature lower than the absorption treatment temperature by 10°C. The atmosphere is preferably vacuum or an inert gas such as Ar or He. The time of aging treatment is from 1 minute to 10 hours, preferably from 10 minutes to 5 hours, and more preferably from 30 minutes
40 to 2 hours.

[0037] It is noted for the machining of the sintered magnet body that if the coolant used in the machining tool is aqueous, or if the surface being machined is exposed to high temperature during the machining, there is a likelihood of an oxide layer forming on the machined surface, which oxide layer can inhibit the absorption reaction of R component from the powder deposit to the magnet body. In such a case, the oxide layer is removable by washing with at least one of alkalis, acids and organic solvents or by shot blasting before adequate absorption treatment is carried out. That is, the sintered magnet body machined to the predetermined shape is washed with at least one agent of alkalis, acids and organic solvents or shot blasted for removing a surface affected layer therefrom before the absorption treatment is carried out.

45 **[0038]** Also, after the absorption treatment or after the aging treatment, the sintered magnet body may be washed with at least one agent selected from alkalis, acids and organic solvents, or machined again. Alternatively, plating or paint coating may be carried out after the absorption treatment, after the aging treatment, after the washing step, or after the machining step following the absorption treatment.

50 **[0039]** Suitable alkalis which can be used herein include potassium pyrophosphate, sodium pyrophosphate, potassium citrate, sodium citrate, potassium acetate, sodium acetate, potassium oxalate, sodium oxalate, etc.; suitable acids include hydrochloric acid, nitric acid, sulfuric acid, acetic acid, citric acid, tartaric acid, etc.; and suitable organic solvents include acetone, methanol, ethanol, isopropyl alcohol, etc. In the washing step, the alkali or acid may be used as an aqueous solution with a suitable concentration not attacking the magnet body.

55 **[0040]** The above-described washing, shot blasting, machining, plating, and coating steps may be carried out by

standard techniques.

[0041] The permanent magnet material of the invention can be used as high-performance permanent magnets.

EXAMPLE

[0042] Examples and Comparative Examples are given below for further illustrating the invention although the invention is not limited thereto. In Examples, the filling factor of alloy powder in the magnet surface-surrounding space is calculated from (a) the dimensional change and weight gain of the magnet after powder treatment and (b) the true density of the powder material.

Example 1 and Comparative Example 1

[0043] An alloy in thin plate form was prepared by a strip casting technique, specifically by weighing predetermined amounts of Nd, Al, Fe and Cu metals having a purity of at least 99% by weight and ferroboron, high-frequency heating in an argon atmosphere for melting, and casting the alloy melt on a copper single roll. The resulting alloy had a composition of 14.5 atom% Nd, 0.5 atom% Al, 0.3 atom% Cu, 5.8 atom% B, and the balance of Fe. The alloy was exposed to hydrogen gas at 0.11 MPa and room temperature for hydriding and then heated up to 500°C for partial dehydriding while evacuating to vacuum. The hydriding pulverization was followed by cooling and sieving, obtaining a coarse powder under 50 mesh.

[0044] On a jet mill using high-pressure nitrogen gas, the coarse powder was finely pulverized to a mass median particle diameter of 4.9 μm. The fine powder was compacted in a nitrogen atmosphere under a pressure of about 1 ton/cm² while being oriented in a magnetic field of 15 kOe. The green compact was then placed in a sintering furnace in an argon atmosphere where it was sintered at 1,060°C for 2 hours, obtaining a magnet block. Using a diamond cutter, the magnet block was machined on all the surfaces to dimensions of 50 mm × 20 mm × 2 mm (thick). It was successively washed with alkaline solution, deionized water, nitric acid, and deionized water, and dried.

[0045] Another alloy in thin plate form was prepared by a strip casting technique, specifically by weighing predetermined amounts of Nd, Dy, Al, Fe, Co and Cu metals having a purity of at least 99% by weight and ferroboron, high-frequency heating in an argon atmosphere for melting, and casting the alloy melt on a copper single roll. The resulting alloy had a composition of 15.0 atom% Nd, 15.0 atom% Dy, 1.0 atom% Al, 2.0 atom% Cu, 6.0 atom% B, 20.0 atom% Fe, and the balance of Co. The alloy was milled on a disc mill in a nitrogen atmosphere into a coarse powder under 50 mesh. On a jet mill using high-pressure nitrogen gas, the coarse powder was finely pulverized to a mass median particle diameter of 8.4 μm. The fine powder thus obtained is designated alloy powder T1.

[0046] Subsequently, 100 g of alloy powder T1 was mixed with 100 g of ethanol to form a suspension, in which the magnet body was immersed for 60 seconds with ultrasonic waves being applied. The magnet body was pulled up and immediately dried with hot air. At this point, alloy powder T1 surrounded the magnet and occupied a space spaced from the magnet surface at an average distance of 56 μm at a filling factor of 30% by volume. The magnet body covered with alloy powder T1 was subjected to absorption treatment in an argon atmosphere at 800°C for 8 hours, then to aging treatment at 500°C for one hour, and quenched, obtaining a magnet body M1 within the scope of the invention. For comparison purposes, a magnet body P1 was prepared by subjecting the magnet body to only heat treatment without powder coverage.

[0047] Magnet bodies M1 and P1 were measured for magnetic properties, which are shown in Table 1. As compared with magnet body P1, magnet body M1 within the scope of the invention showed an increase of 183 kAm in coercive force and a drop of 15 mT in remanence.

Table 1

	Designation	B _r [T]	H _{cJ} [kAm ⁻¹]	(BH) _{max} [kJ/m ³]
Example 1	M1	1.390	1178	374
Comparative Example 1	P1	1.405	995	381

Example 2 and Comparative Example 2

[0048] An alloy in thin plate form was prepared by a strip casting technique, specifically by weighing predetermined amounts of Nd, Al and Fe metals having a purity of at least 99% by weight and ferroboron, high-frequency heating in an argon atmosphere for melting, and casting the alloy melt on a copper single roll. The resulting alloy had a composition of 13.5 atom% Nd, 0.5 atom% Al, 6.0 atom% B, and the balance of Fe. The alloy was exposed to hydrogen gas at 0.11 MPa and room temperature for hydriding and then heated up to 500°C for partial dehydriding while evacuating to vacuum.

The hydriding pulverization was followed by cooling and sieving, obtaining a coarse powder under 50 mesh (designated alloy powder A).

[0049] Another alloy was prepared by weighing predetermined amounts of Nd, Dy, Fe, Co, Al and Cu metals having a purity of at least 99% by weight and ferroboron, high-frequency heating in an argon atmosphere for melting, and casting in a flat mold. The resulting ingot had a composition of 20 atom% Nd, 10 atom% Dy, 24 atom% of Fe, 6 atom% B, 1 atom% Al, 2 atom% Cu, and the balance of Co. The ingot was crushed on a jaw crusher and a Brown mill in a nitrogen atmosphere, followed by sieving, obtaining a coarse powder under 50 mesh (designated alloy powder B).

[0050] Subsequently, alloy powders A and B were weighed in amounts of 90% and 10% by weight, respectively, and mixed together on a V blender for 30 minutes. On a jet mill using high-pressure nitrogen gas, the mixed powder was finely pulverized to a mass median particle diameter of 4.3 μm . The mixed fine powder was compacted in a nitrogen atmosphere under a pressure of about 1 ton/cm² while being oriented in a magnetic field of 15 kOe. The green compact was then placed in a sintering furnace in an argon atmosphere where it was sintered at 1,060°C for 2 hours, obtaining a magnet block. Using a diamond cutter, the magnet block was machined on all the surfaces to dimensions of 40 mm \times 12 mm \times 4 mm (thick). It was successively washed with alkaline solution, deionized water, nitric acid, and deionized water, and dried.

[0051] Another alloy in thin plate form was prepared by a strip casting technique, specifically by weighing predetermined amounts of Nd, Dy, Al, Fe, Co and Cu metals having a purity of at least 99% by weight, ferroboron and retort carbon, high-frequency heating in an argon atmosphere for melting, and casting the alloy melt on a copper single roll. The resulting alloy had a composition of 10.0 atom% Nd, 20.0 atom% Dy, 1.0 atom% Al, 1.0 atom% Cu, 5.0 atom% B, 1.0 atom% C, 15.0 atom% Fe, and the balance of Co. The alloy was milled on a disc mill in a nitrogen atmosphere into a coarse powder under 50 mesh. On a jet mill using high-pressure nitrogen gas, the coarse powder was finely pulverized to a mass median particle diameter of 6.7 μm . The fine powder thus obtained is designated alloy powder T2.

[0052] Subsequently, 100 g of alloy powder T2 was mixed with 100 g of ethanol to form a suspension, in which the magnet body was immersed for 60 seconds with ultrasonic waves being applied. The magnet body was pulled up and immediately dried with hot air. At this point, alloy powder T2 surrounded the magnet and occupied a space spaced from the magnet surface at an average distance of 100 μm at a filling factor of 25% by volume. The magnet body covered with alloy powder T2 was subjected to absorption treatment in an argon atmosphere at 850°C for 15 hours, then to aging treatment at 510°C for one hour, and quenched, obtaining a magnet body M2 within the scope of the invention. For comparison purposes, a magnet body P2 was prepared by subjecting the magnet body to only heat treatment without powder coverage.

[0053] Magnet bodies M2 and P2 were measured for magnetic properties, which are shown in Table 2. As compared with magnet body P2, magnet body M2 within the scope of the invention showed an increase of 167 kAm in coercive force and a drop of 13 mT in remanence.

Table 2

	Designation	B _r [T]	H _{cJ} [kAm ⁻¹]	(BH) _{max} [kJ/m ³]
Example 2	M2	1.399	1297	378
Comparative Example 2	P2	1.412	1130	385

Example 3 and Comparative Example 3

[0054] An alloy in thin plate form was prepared by a strip casting technique, specifically by weighing predetermined amounts of Nd, Pr, Al and Fe metals having a purity of at least 99% by weight and ferroboron, high-frequency heating in an argon atmosphere for melting, and casting the alloy melt on a copper single roll. The resulting alloy had a composition of 12.5 atom% Nd, 1.5 atom% Pr, 0.5 atom% Al, 5.8 atom% B, and the balance of Fe. The alloy was exposed to hydrogen gas at 0.11 MPa and room temperature for hydriding and then heated up to 500°C for partial dehydriding while evacuating to vacuum. The hydriding pulverization was followed by cooling and sieving, obtaining a coarse powder under 50 mesh.

[0055] On a jet mill using high-pressure nitrogen gas, the coarse powder was finely pulverized to a mass median particle diameter of 4.4 μm . The fine powder was compacted in a nitrogen atmosphere under a pressure of about 1 ton/cm² while being oriented in a magnetic field of 15 kOe. The green compact was then placed in a sintering furnace in an argon atmosphere where it was sintered at 1,060°C for 2 hours, obtaining a magnet block. Using a diamond cutter, the magnet block was machined on all the surfaces to dimensions of 50 mm \times 50 mm \times 8 mm (thick). It was successively washed with alkaline solution, deionized water, nitric acid, and deionized water, and dried.

[0056] Another alloy in thin plate form was prepared by a strip casting technique, specifically by weighing predetermined amounts of Nd, Dy, Al, Fe, Co and Cu metals having a purity of at least 99% by weight and ferroboron, high-frequency

heating in an argon atmosphere for melting, and casting the alloy melt on a copper single roll. The resulting alloy had a composition of 10.0 atom% Nd, 20.0 atom% Dy, 1.0 atom% Al, 1.0 atom% Cu, 6.0 atom% B, 15.0 atom% Fe, and the balance of Co. The alloy was exposed to hydrogen gas at 0.11 MPa and room temperature for hydriding and then heated up to 350°C for partial dehydriding while evacuating to vacuum. The hydriding pulverization was followed by cooling and sieving, obtaining a coarse powder under 50 mesh. It contained hydrogen in an atom ratio of 58 relative to 100 for the alloy, that is, a hydrogen content of 36.71 atom%. On a jet mill using high-pressure nitrogen gas, the coarse powder was finely pulverized to a mass median particle diameter of 4.2 μm. The fine powder thus obtained is designated alloy powder T3.

[0057] Subsequently, 100 g of alloy powder T3 was mixed with 100 g of isopropyl alcohol to form a suspension, in which the magnet body was immersed for 60 seconds with ultrasonic waves being applied. The magnet body was pulled up and immediately dried with hot air. At this point, alloy powder T3 surrounded the magnet and occupied a space spaced from the magnet surface at an average distance of 65 μm at a filling factor of 30% by volume. The magnet body covered with alloy powder T3 was subjected to absorption treatment in an argon atmosphere at 850°C for 12 hours, then to aging treatment at 535°C for one hour, and quenched, obtaining a magnet body M3 within the scope of the invention. For comparison purposes, a magnet body P3 was prepared by subjecting the magnet body to only heat treatment without powder coverage.

[0058] Magnet bodies M3 and P3 were measured for magnetic properties, which are shown in Table 3. As compared with magnet body P3, magnet body M3 within the scope of the invention showed an increase of 183 kAm in coercive force and a drop of 13 mT in remanence.

Table 3

	Designation	B_r [T]	H_{cJ} [kAm ⁻¹]	$(BH)_{max}$ [kJ/m ³]
Example 3	M3	1.412	1225	386
Comparative Example 3	P3	1.425	1042	394

Example 4 and Comparative Example 4

[0059] An alloy in thin plate form was prepared by a strip casting technique, specifically by weighing predetermined amounts of Nd, Al and Fe metals having a purity of at least 99% by weight and ferroboron, high-frequency heating in an argon atmosphere for melting, and casting the alloy melt on a copper single roll. The resulting alloy had a composition of 13.5 atom% Nd, 0.5 atom% Al, 6.0 atom% B, and the balance of Fe. The alloy was exposed to hydrogen gas at 0.11 MPa and room temperature for hydriding and then heated up to 500°C for partial dehydriding while evacuating to vacuum. The hydriding pulverization was followed by cooling and sieving, obtaining a coarse powder under 50 mesh (designated alloy powder C).

[0060] Another alloy was prepared by weighing predetermined amounts of Nd, Dy, Fe, Co, Al and Cu metals having a purity of at least 99% by weight and ferroboron, high-frequency heating in an argon atmosphere for melting, and casting in a flat mold. The resulting ingot had a composition of 20 atom% Nd, 10 atom% Dy, 24 atom% Fe, 6 atom% B, 1 atom% Al, 2 atom% Cu, and the balance of Co. The ingot was crushed on a jaw crusher and a Brown mill in a nitrogen atmosphere, followed by sieving, obtaining a coarse powder under 50 mesh (designated alloy powder D).

[0061] Subsequently, alloy powders C and D were weighed in amounts of 90% and 10% by weight, respectively, and mixed together on a V blender for 30 minutes. On a jet mill using high-pressure nitrogen gas, the mixed powder was finely pulverized to a mass median particle diameter of 5.2 μm. The mixed fine powder was compacted in a nitrogen atmosphere under a pressure of about 1 ton/cm² while being oriented in a magnetic field of 15 kOe. The green compact was then placed in a sintering furnace in an argon atmosphere where it was sintered at 1,060°C for 2 hours, obtaining a magnet block. Using a diamond cutter, the magnet block was machined on all the surfaces to dimensions of 40 mm × 12 mm × 4 mm (thick). It was successively washed with alkaline solution, deionized water, nitric acid, and deionized water, and dried.

[0062] Another alloy in thin plate form was prepared by a strip casting technique, specifically by weighing predetermined amounts of Nd, Dy, Al, Fe, Co and Cu metals having a purity of at least 99% by weight and ferroboron, high-frequency heating in an argon atmosphere for melting, and casting the alloy melt on a copper single roll. The resulting alloy had a composition of 10.0 atom% Nd, 20.0 atom% Dy, 1.0 atom% Al, 1.0 atom% Cu, 6.0 atom% B, 15.0 atom% Fe, and the balance of Co. The alloy was milled on a disc mill in a nitrogen atmosphere into a coarse powder under 50 mesh. On a jet mill using high-pressure nitrogen gas, the coarse powder was finely pulverized to a mass median particle diameter of 8.4 μm. The fine powder thus obtained is designated alloy powder T4.

[0063] Subsequently, 70 g of alloy powder T4 was mixed with 30 g of dysprosium fluoride and 100 g of ethanol to

form a suspension, in which the magnet body was immersed for 60 seconds with ultrasonic waves being applied. Note that the dysprosium fluoride powder had an average particle size of 2.4 μm . The magnet body was pulled up and immediately dried with hot air. At this point, alloy powder T4 surrounded the magnet and occupied a space spaced from the magnet surface at an average distance of 215 μm at a filling factor of 15% by volume. The magnet body covered with alloy powder T4 and dysprosium fluoride powder was subjected to absorption treatment in an argon atmosphere at 825°C for 10 hours, then to aging treatment at 500°C for one hour, and quenched, obtaining a magnet body M4 within the scope of the invention. For comparison purposes, a magnet body P4 was prepared by subjecting the magnet body to only heat treatment without powder coverage.

[0064] Magnet bodies M4 and P4 were measured for magnetic properties, which are shown in Table 4. As compared with magnet body P4, magnet body M4 within the scope of the invention showed an increase of 294 kAm in coercive force and a drop of 15 mT in remanence.

Table 4

	Designation	B_r [T]	H_{cJ} [kAm ⁻¹]	$(BH)_{max}$ [kJ/m ³]
Example 4	M4	1.397	1424	378
Comparative Example 4	P4	1.412	1130	386

Examples 5 to 18 and Comparative Example 5

[0065] An alloy in thin plate form was prepared by a strip casting technique, specifically by weighing predetermined amounts of Nd, Al, Fe and Cu metals having a purity of at least 99% by weight and ferroboron, high-frequency heating in an argon atmosphere for melting, and casting the alloy melt on a copper single roll. The resulting alloy had a composition of 14.5 atom% Nd, 0.5 atom% Al, 0.3 atom% Cu, 5.8 atom% B, and the balance of Fe. The alloy was exposed to hydrogen gas at 0.11 MPa and room temperature for hydriding and then heated up to 500°C for partial dehydriding while evacuating to vacuum. The hydriding pulverization was followed by cooling and sieving, obtaining a coarse powder under 50 mesh.

[0066] On a jet mill using high-pressure nitrogen gas, the coarse powder was finely pulverized to a mass median particle diameter of 4.5 μm . The fine powder was compacted in a nitrogen atmosphere under a pressure of about 1 ton/cm² while being oriented in a magnetic field of 15 kOe. The green compact was then placed in a sintering furnace in an argon atmosphere where it was sintered at 1,060°C for 2 hours, obtaining a magnet block. Using a diamond cutter, the magnet block was machined on all the surfaces to dimensions of 5 mm \times 5 mm \times 2.5 mm (thick). It was successively washed with alkaline solution, deionized water, citric acid, and deionized water, and dried.

[0067] Another alloy in thin plate form was prepared by a strip casting technique, specifically by weighing predetermined amounts of Nd, Dy, Al, Fe, Co, Cu, Si, Ti, V, Cr, Mn, Ni, Ga, Ge, Zr, Nb, Mo, Hf, Ta and W metals having a purity of at least 99% by weight and ferroboron, high-frequency heating in an argon atmosphere for melting, and casting the alloy melt on a copper single roll. The resulting alloy had a composition of 15.0 atom% Nd, 15.0 atom% Dy, 1.0 atom% Al, 2.0 atom% Cu, 6.0 atom% B, 2.0 atom% E (= Si, Ti, V, Cr, Mn, Ni, Ga, Ge, Zr, Nb, Mo, Hf, Ta or W), 20.0 atom% Fe, and the balance of Co. The alloy was milled on a disc mill in a nitrogen atmosphere into a coarse powder under 50 mesh. On a jet mill using high-pressure nitrogen gas, the coarse powder was finely pulverized to a mass median particle diameter of 8.0-8.8 μm . The fine powder thus obtained is designated alloy powder T5.

[0068] Subsequently, 100 g of alloy powder T5 was mixed with 100 g of ethanol to form a suspension, in which the magnet body was immersed for 60 seconds with ultrasonic waves being applied. The magnet body was pulled up and immediately dried with hot air. At this point, alloy powder T5 surrounded the magnet and occupied a space spaced from the magnet surface at an average distance of 83 to 97 μm at a filling factor of 25 to 35% by volume.

[0069] The magnet body covered with alloy powder T5 was subjected to absorption treatment in an argon atmosphere at 800°C for 8 hours, then to aging treatment at 490 to 510°C for one hour, and quenched, obtaining a magnet body within the scope of the invention. The magnet bodies are designated M5-1 to M5-14 corresponding to the additive element (in the alloy powder) E = Si, Ti, V, Cr, Mn, Ni, Ga, Ge, Zr, Nb, Mo, Hf, Ta and W. For comparison purposes, a magnet body P5 was prepared by subjecting the magnet body to only heat treatment without powder coverage.

[0070] Magnet bodies M5-1 to M5-14 and P5 were measured for magnetic properties, which are shown in Table 5. As compared with magnet body P5, magnet bodies M5-1 to M5-14 within the scope of the invention showed an increase of 170 kAm or more in coercive force and a drop of 33 mT or less in remanence.

Table 5

	Designation	B_r [T]	H_{cJ} [kAm ⁻¹]	$(BH)_{max}$ [kJ/m ³]	
5	Example 5	M5-1	1.400	1194	379
	Example 6	M5-2	1.388	1180	373
	Example 7	M5-3	1.390	1210	373
10	Example 8	M5-4	1.389	1238	373
	Example 9	M5-5	1.382	1165	369
	Example 10	M5-6	1.380	1179	369
	Example 11	M5-7	1.378	1290	368
15	Example 12	M5-8	1.398	1206	378
	Example 13	M5-9	1.400	1177	379
	Example 14	M5-10	1.387	1186	372
20	Example 15	M5-11	1.372	1202	365
	Example 16	M5-12	1.382	1178	369
	Example 17	M5-13	1.372	1174	364
	Example 18	M5-14	1.378	1183	367
25	Comparative Example 5	P5	1.405	995	383

Examples 19 to 22

30 **[0071]** The magnet body M1 of 50 mm × 20 mm × 2 mm (thick) in Example 1 was washed with 0.5N nitric acid for 2 minutes, rinsed with deionized water, and immediately dried with hot air. This magnet body within the scope of the invention is designated M6. Separately, the 50 × 20 mm surface of magnet body M1 was machined by means of a surface grinding machine, obtaining a magnet body of 50 mm × 20 mm × 1.6 mm (thick). This magnet body within the scope of the invention is designated M7. The magnet bodies M7 were subjected to epoxy coating and copper/nickel electroplating, obtaining magnet bodies M8 and M9, respectively, which are also within the scope of the invention.

35 **[0072]** Magnet bodies M6 to M9 were measured for magnetic properties, which are shown in Table 6. All magnet bodies exhibit excellent magnetic properties.

Table 6

	Designation	B_r [T]	H_{cJ} [kAm ⁻¹]	$(BH)_{max}$ [kJ/m ³]	
40	Example 19	M6	1.395	1180	376
	Example 20	M7	1.385	1178	370
45	Example 21	M8	1.387	1176	371
	Example 22	M9	1.385	1179	371

50 **[0073]** In respect of numerical ranges disclosed herein it will of course be understood that in the normal way the technical criterion for the upper limit is different from the technical criterion for the lower limit, i.e. the upper and lower limits are intrinsically distinct proposals.

Claims

55 1. A method of preparing a rare earth permanent magnet material, comprising the steps of:

(i) disposing a powder on a surface of a sintered magnet body of R¹-Fe-B composition wherein R¹ is at least one element selected from rare earth elements, Sc and Y;

said powder comprising at least 30% by weight of an alloy R²_aT_bM_cA_dH_e wherein

R² is at least one element selected from rare earth elements, Sc and Y,

T is iron and/or cobalt, M is one or more elements selected from Al, Cu, Zn, In, Si, P, S, Ti, V, Cr, Mn, Ni, Ga, Ge, Zr, Nb, Mo, Pd, Ag, Cd, Sn, Sb, Hf, Ta, and W, A is boron and/or carbon, H is hydrogen, and

"a" to "e", indicative of atomic percentages based on the alloy, are in the ranges 15 ≤ a ≤ 80, 0.1 ≤ c ≤ 15, 0 ≤ d ≤ 30, 0 ≤ e ≤ (ax2.5) with "b" making up the balance,

said powder having an average particle size equal to or less than 100 μm;

(ii) heat treating the magnet body having the powder disposed on its surface at a temperature equal to or below the sintering temperature of the magnet body, in vacuum or in an inert gas, for absorption treatment causing R² and at least one of T, M and A in the powder to be absorbed into the magnet body.

2. The method of claim 1, wherein the sintered magnet body has a minimum portion with a dimension equal to or less than 20 mm.

3. The method of claim 1 or 2, wherein said powder is disposed on the magnet body surface in an amount corresponding to an average filling factor of at least 10% by volume in a magnet body-surrounding space at a distance equal to or less than 1 mm from the magnet body surface.

4. The method of claim 1, 2 or 3, wherein said powder contains at least 1% by weight of at least one of an oxide of R³, a fluoride of R⁴, and an oxyfluoride of R⁵ wherein each of R³, R⁴, and R⁵ is at least one element selected from rare earth elements inclusive of Sc and Y, so that at least one of R³, R⁴, and R⁵ is absorbed in the magnet body.

5. The method of claim 4, wherein each or any of said R³, R⁴ and/or R⁵ in the powder contains at least 10 atom% of at least one element selected from Nd, Pr, Dy and Tb.

6. The method of any one of claims 1 to 5, further comprising, after the absorption treatment, effecting aging treatment at a lower temperature.

7. The method of any one of claims 1 to 6, wherein R² contains at least 10 atom% of at least one element selected from Nd, Pr, Dy, and Tb.

8. The method of any one of claims 1 to 7, wherein for said disposal on the magnet body, the powder is fed dispersed as slurry in an aqueous or organic solvent.

9. The method of any one of claims 1 to 8, further comprising, prior to the disposing step, washing the magnet body with at least one agent selected from alkalis, acids, and organic solvents.

10. The method of any one of claims 1 to 9, further comprising, prior to the disposing step, shot blasting the magnet body for removing a surface layer.

11. The method of any one of claims 1 to 10, further comprising washing the magnet body with at least one agent selected from alkalis, acids, and organic solvents after the absorption treatment or after the aging treatment.

12. The method of any one of claims 1 to 11, further comprising machining the magnet body after the absorption treatment or after the aging treatment.

13. The method of any one of claims 1 to 12, further comprising plating or coating the magnet body, after the absorption treatment, after the aging treatment, after the alkali, acid or organic solvent washing step following the aging treatment, or after the machining step following the aging treatment.

REFERENCES CITED IN THE DESCRIPTION

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